ELECTROLYTIC RECOVERY OF SODIUM FROM SODIUM-CONTAINING ORGANOALUMINUM COMPOUNDS

K. Ziegler, H. Lehmkuhl and W. Grimme

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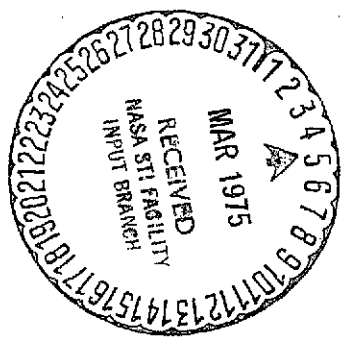

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16. Abstract

Molten $NaAlEt_4$ or a related org. complex is electrolyzed in an inert gas at 100-160° in a closed cylindrical cell of enameled sheet steel, with a central cathode and a concentric anode of Fe or Cu gauze. Molten Na collects on the cathode, trickles downwardly, and collects in the bottom of the cell. The complex radical seps. at the anode, where it is decompd. into Et_3Al and a mixt. of equal vols. C_2H_4 and C_2H_6 (or analogous products from other complexes). If the Et_3Al is permitted to diffuse to the cathode, it reacts with the sepd. Na, exchanging Al for Na in regenerating electrolyte.

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ELECTROLYTIC RECOVERY OF SODIUM FROM SODIUM-CONTAINING ORGANOALUMINUM COMPOUNDS

Reported by Dr. Karl Ziegler
Dr. Karl Ziegler, Dr. Herbert Lehmkuhl, and Dr. Wolfram Grimme are named as inventors.

Federal Republic of Germany,
German Patent Office
Patent No. 1,114, 330

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ABSTRACT: Molten $NaAlEt_4$ or a related organic complex is electrolyzed in an inert gas at 100-160° in a closed cylindrical cell of enameled sheet steel, with a central cathode and a concentric anode of Fe or Cu gauze. Molten Na collects on the cathode, trickles downward, and collects in the bottom of the cell. The complex radical separates at the anode, where it is decomposed into Et_3Al and a mixture of equal volumes of C_2H_4 and C_2H_6 (or analogous products from other complexes). If the Et_3Al is permitted to diffuse to the cathode, it reacts with the separated Na, exchanging Al for Na in regenerating electrolyte. This loss of Na may be avoided in several ways: (1) If the electrolyte contains 5% $NaAl(Et_3)OBu$, continuously replenished during electrolysis, the Et_2AlOBu formed at the anode is insoluble in the electrolyte, separates as a liquid layer, and may be reconverted into $NaAl(Et_3)OBu$ by reaction with NaH and C_2H_4. (2) A diaphragm of paper or fabric, supported on a porous cylinder, is interposed between anode and cathode; by maintaining the liquid in the cathode compartment at a higher level than that in the anode compartment, the liquid may be caused to flow continuously through the diaphragm, thus preventing diffusion in the opposite direction. If the electrolyte

is $NaAlEt_4$, with Pb granules filling the anode compartment, or if the electrolyte is $NaAlBu_4$, with Al granules, the liquid issuing from the anode compartment will contain up to 10% Bu_3Al or Et_4Pb, which may be removed by distillation in vacuo.
(3) The electrolyte may be $NaAl(Et_3)H$; the anode gas is then H, which may be used to regenerate the electrolyte from Et_3Al, recovered by distillation in vacuo.
(4) With a modified cell, the anode may be impure Na or 1% Na amalgam; Na collects on a nonconductive gauze beneath the cathode. To increase the conductivity, as much as 80% of the $NaAlEt_4$ may be replaced by $KAlEt_4$ (formed by reaction with KCl at 150°) without deposition of K at the cathode. The currend density is 10-50 amperes per square decimeter at 0.5-5 volts, and the yield is 100%.

The winning of metallic sodium by cathodic deposition / 1* of the metal in electrolysis of sodium-containing compounds is well known. Here, we must differentiate between two different types of sodium winning. In one form, fused salt electrolyses are performed with sodium hydroxide or sodium chloride, with the melting point lowered by addition of calcium chloride. This procedure, of course, requires relatively high electrolysis temperatures, particularly in electrolysis of sodium chloride.

In the other process for winning sodium, metallic sodium is first dissolved as an amalgam in a mercury cathode by electrolysis of warm sodium chloride solution. This amalgam must be freed of its sodium content in a secondary electrolysis, in which it is connected as the anode and the metallic sodium is deposited cathodically. One cannot work in the presence of water in this secondary electrolysis. Instead, a melt of sodium hydroxide, sodium iodide and sodium bromide is used as the electrolyte. The bath temperature is about 250°C. At this high temperature it is impossible to prevent the mercury from entering the metallic sodium, probably because the vapor pressure of the

*Translator's Note: Numbers in margin indicate pagination of original foreign text.

mercury is already very high at the necessary high temperature. The fused electrolyte becomes saturated with this mercury vapor, and the sodium at the cathode then takes up this proportion of mercury again. The separated sodium from the secondary electrolysis must then be freed of mercury, not because of the usefulness of the sodium, but for economic reasons, because the loss of mercury would not be acceptable. This purification is done by an additional treatment with some metallic calcium. The calcium binds the mercury in a solid calcium amalgam, from which one can pour off the fused mercury-free sodium. The mercury can be recovered from the calcium amalgam, by decomposition with acids, for instance. Over all, this procedure is complex, and it requires many steps. / 2

F. Hein et al. have previously described the electrolysis of sodium aluminum tetraethyl (Zeitschr. anorg. allg. Chemie, 141[1924], p. 161 ff.). If one studies the cathodic reaction products obtained in the electrolysis, which were not characterized by F. Hein, one finds that one always obtains spongy mixtures of sodium and aluminum, and that the ratio of sodium to aluminum depends on the current density and the duration of electrolysis. This finding is easily understood if one considers the reaction mechanism for the electrolytic decomposition of the $NaAl(C_2H_5)_4$:

$$3\,NaAl(C_2H_5)_4 \xrightarrow{\text{electrical energy}} 3\,Na + 3\,Al(C_2H_5)_3 + 3\,\{C_2H_5\}$$

Sodium aluninum tetraethyl melts at 130°C. Under the conditions of fused electrolysis at at least 130°C, however, the cathodically formed sodium reacts rapidly with the triethyl aluminum, which is not complexly bound, and which dissolves in the sodium aluminum tetraethyl. Some 16% of $AlEt_3$ dissolves in $NaAlEt_4$ at 130°C. This causes re-formation

of sodium aluminum tetraethyl and Al:

$$3\,Na + 4\,Al(C_2H_5)_3 \rightarrow 3\,NaAl(C_2H_5)_4 + Al$$

The aluminum deposits on the cathode. The ratio of sodium to aluminum on the cathode depends only on the rate of diffusion of $AlEt_3$ to the cathode and, therefore, on the current density and the stirring in the electrolyte. But in no case is it possible, without special measures, to deposit solely or even predominantly sodium. In general, one gets mixtures of sodium and aluminum in the molar ratio of 1:1. This fact follows from the reaction mechanism of the electrolysis: / 3

$$3\,NaAl(C_2H_5)_4 \xrightarrow{\text{electrical energy}} 3\,Na + 3\,Al(C_2H_5)_3 + 3\,(C_2H_5)$$
$$^9/_4\,Na + 3\,Al(C_2H_5)_3 \longrightarrow {}^9/_4\,NaAl(C_2H_5)_4 + {}^3/_4\,Al$$

That is, 3/4 Na and 3/4 Al appear at the cathode.

The invention concerns a new process for electrolytic separation of sodium which produces simplifications and improvements over the state of the technology in many respects. The process is particularly suitable for the cathodic deposition of pure sodium which contains only traces of contaminants (maximum of 1 γ foreign metal per gram of sidium).

The object of the invention is a process for cathodic deposition of sodium through electrolysis of sodium-containing organic aluminum compounds in an inert atmosphere. It is characterized by the fact that a melt of complex compounds of the general formula $MeAlR_3R'$, in which Me is sodium or a mixture of sodium and potassium, R is an alkyl residue, and R' is hydrogen, an alkyl, an alkoxy, and/or a perhaps substituted aryloxy residue, is electrolyzed.

Reaction of the anodically formed, non-complexly bound metal alkyls with the cathodically separated sodium is prevented, as by use of a diaphragm, by electrolysis in vacuum, or by addition of compounds of the general formula MeAl R_3OR'', in which general formula Me and R have the meaning given before and R" is an alkyl, a cycloalkyl, a phenyl, or an alkyl-substituted phenyl residue.

In particular, suitable electrolytes for performing the process according to the invention are those complex compounds of the general formula given in which R is a straight-chain alkyl residue with preferably 2 to 6, and especially 2, carbon atoms, and R' is hydrogen, a straight-chain alkyl residue with preferably 2 to 6, and especially 2 carbon atoms, or an organic residue OR" in which R" is an alkyl, a cycloalkyl, a phenyl, or an alkyl-substituted phenyl residue. Electrolytes in which R' is hydrogen are practically useful only in certain design forms of the invention, which will be considered later.

It was found that one of the essential prerequisites for the deposition of pure sodium at the cathode is the condition that one use aluminum complex compounds as the electrolyte which are sufficiently resistant in the melt at the bath temperature; that is, they are not decomposed into their individual components (free aluminum alkyl compound and complex former) to the extent that the deposition of pure sodium is disturbed, and/or which do not react with sodium at the electrolysis temperatures used. This basic requirement for the process according to the invention is fulfilled by the specified compounds with the general formula MeAl R_3R'.

Because of the sensitivity of the electrolyte to air and water, all operations must be performed in an inert gas atmosphere of nitrogen or argon, for example, to exclude moisture. /4

In one of the embodiments of the invention which is simplest to use, the electrolysis is done at electrodes which do not participate in the chemical conversions of the electrolysis. That is, both cathode and anode consist of indifferent metals, such as copper, iron, nickel or other indifferent metals. Alloys such as brass are also usable. In this case, sodium is deposited cathodically, while the gaseous decomposition product of the ethyl residue appears at the anode. If the complex compound $MeAlR_4$ is used as the electrolyte (that is, an aluminum tetraalkyl complex compound), one aluminum trialkyl appears at the anode simultaneously with every metal equivalent deposited. If it did not prevent mixing of the aluminum trialkyl formed with the cathodically deposited sodium, the trialkyl aluminum would diffuse through the electrolyte to the cathode. After a short time it would disturb the deposition of sodium, with simultaneous deposition of aluminum.

According to the invention, then, mixing of the anodically formed free metal alkyl with the cathodically deposited sodium is prevented. There are basically two different possibilities for this, the use of mechanical or physical aids which exclude such undesired mixing, and a conscious control of the chemical processes in the electrolyte, which also prevents an undesired back-reaction with participation of the deposited sodium.

The particular mechanical or physical aids are:

a) placing of a diaphragm between the anode and cathode; or
b) performance of the electrolysis in a vacuum, so that the anodically formed metal alkyls distill directly out of the electrolytic liquid before they can migrate through the electrolyte to the cathode. In this embodiment, it is not practical to use indifferent anodes, because large

amounts of gas are formed continuously at the anode and must be pumped off. This form is suitable for the use of anodes at which the ethyl residue does not decompose, but is bound in metal alkyl compounds.

If one works with a diaphragm between the cathode and anode, then it may be practical to maintain a particularly weak flow of liquid from the cathode space into the anode space. This can be simply done, for instance, by keeping the liquid level in the cathode space somewhat higher than in the anode space, so that the desired steady flow is maintained by the natural liquid exchange through the diaphragm. If necessary, it is also possible to work with more diaphragms -- for instance, two. / 5

Pressed fibrous materials such as asbestos, glass wool and quartz wool are suitable diaphragm materials. Diaphragms can also be made of porous cellulose products -- for instance, of filter paper condensed for reduction of pore sizes, or chemically imprgenated, which can be clamped between cloths of cotton.

If, on the other hand, the electrolysis is done in a vacuum cell, then in general very low pressures are required in the cell. For example, work can be done satisfactorily at pressures below 1 mm Hg. It happens that the free metal alkyl compounds formed must be distilled away so rapidly that certain maximum concentrations of these alkyl compounds in the electrolyte are not exceeded. For aluminum triethyl this is some 3%, and preferably some 1%. Electrolysis systems with which the process of the invention can be performed, and in which both the use of the mentioned diaphragms and operation under vacuum are explained, are described, for instance, in the French patents 1,139,719, 1,208,430 and 1,222,643.

The other possibility of preventing the undesired back reaction by control of the chemical processes in the electrolyte can also be realized in various ways. For instance, if triethyl aluminum is liberated at the anode during the electrolysis, it can be separated from the reaction with sodium in one embodiment of the invented process by addition of alkoxy or aryloxy complex compounds with the general formula $MeAl\ R_3OR"$ in which Me, R and R" have the stated meaning. In this case the free aluminum trialkyl is converted into the sodium aluminum tetraalkyl compound, i. e., into one of the electrolytes which can be used according to the invention, while at the same time free aluminum compounds of the general formula $AlR_2OR"$ are formed. It appears, surprisingly, that in this form of the process, an undesired back reaction does not occur. Although free aluminum trialkyl with sodium decomposes even at temperatures of about 100°C, such a decomposition does not occur with an alkoxy or aryloxy aluminum dialkyl and metallic sodium in the temperature range which is suitable for carrying out the process of the invention, i. e., at temperatures of about 150 to 160°C. Undesired conversion occurs only if the temperature goes above this limit. The addition of the complex compound $MeAlR_3OR"$ can be intermittent, as at the beginning of the electrolysis, in sufficient amount, or, preferably, continuously in the required amount during the electrolysis.

Thus, if one continuously converts any portion of free trialkyl aluminum into the corresponding alkoxy or aryloxy aluminum dialkylcompounds by preferably continuous addition of the $MeAlR_3OR"$ compounds, one can deposit pure sodium cathodically up to some 150°C. To carry out this embodiment / 6
of the invention, it is possible not only to use $MeAlR_4$ as the principal electrolyte with addition of at least the necessary amounts of $MeAlR_3OR"$, but also to use this second complex compound as the sole electrolyte. But use of the

tetrallkyl complex as the principal electrolyte is preferred because of the relatively poor electrical conductivity of the alkoxy complex compounds.

If still other metal alkyl compounds are formed, which do not react with the aluminum alkoxy complex compound, then it is essential to use mechanical aids to separate the anodic reaction products from the cathodically deposited metal.

Of the compounds having the general formula $MeAlR_3R'$ which are to be used as electrolytes according to the invention, the compounds in which Me is potassium have significantly better conductivity than the corresponding sodium compounds. At the same time it has appeared that if one electrolyzes a mixture of the potassium and sodium tetralkyl complex compounds, pure sodium is deposited as long as the potassium proportion does not exceed 80% of the alkali metal. For this reason it is preferred to use mixtures of sodium and potassium complex compounds of the general formula $MeAlR_3R'$ as electrolytes. While the electrolysis proceeds, the sodium compound in the electrolyte is used up. This must then be added in the appropriate amount either intermittently or continuously so that the potassium proportion does not exceed 80%.

Even when working without the potassium compound, the part of the sodium aluminum complex compound decomposed during the electrolysis must be replaced intermittently or continuously to carry out a continuous process. If one works with mechanical aids to eliminate the anodically formed trialkyl aluminum, it is convenient to reuse this to produce the sodium aluminum tetraalkyl compound. For this purpose, it in conducted into a pressure reactor along with fresh sodium,

and converted back to the electrolyte compound by treatment with hydrogen and then with the appropriate olefin. For instance, the process described in German Patent 917006 is suitable for this conversion. In this way it is possible to carry out cyclic processes, such as for refining sodium, in which the sodium to be purified is introduced to the cycle in the regeneration of the electrolyte, and the purified metal is removed cathodically.

Even if one converts the free trialkyl aluminum compounds formed into the free alkoxy or aryloxy aluminum dialkyl compounds within the electrolyte by the addition of $MeAlR_3OR''$, such cyclic processes can be used. In this case the compounds with the formula AlR_2OR'' are converted back to the $MeAlR_3OR''$ compounds outside the electrolysis cell. These are then returned as new electrolyte, or for reaction with the trialkyl aluminum compounds in the electrolyte. The best possibility for regenerating compounds with the general formula $MeAl_3OR''$ consists of reacting compounds having the formula R_2AlOR'' with the alkali metal hydride and the corresponding olefins, such as ethylene. Treatment with the olefins can be done at 130 to 220°C, preferably 150 to 200°C, and at pressures up to 100 atm., preferably 1 to 20 atm. / 7

Deposition of pure sodium over an arbitrarily long period of electrolysis is also possible with another and especially preferred embodiment. According to this preferred embodiment of the invention, the electrolysis melt is electrolyzed with compounds of the general formula $MeAlR_3R'$ with a cathode of an indifferent metal and a sodium-containing anode. Surprisingly, it appears that in the simplest possible way this maintains the conditions for carrying out the process of the invention over an arbitrarily long period.

While the decomposition product of the remaining electrolyte residue appears along with the liberated trialkyl aluminum at an indifferent electrode, when a sodium-containing electrode is used with the same conditions, this free residue dissolves sodium going into solution anodically, forming alkyl sodium, for instance. As an equivalent amount of trialkyl aluminum is simultaneously liberated at the anode and this reacts immediately with the sodium compound just formed at the anode, giving the sodium aluminum complex compound, this procedure continuously maintains a constant electrolyte composition. No mechanical aid of any sort need be used to prevent undesired back-reactions, and no intermittent or continuous supplementation of the electrode consumed is needed.

Various sodium-containing materials can be used as the anode material here. For instance, melted crude sodium is suitable. This is the simplest form of carrying out the process of the invention. But other anode materials are also usable.

Use of sodium amalgam as the anode material is especially preferred. This sodium amalgam appears in large amounts in the electrolysis of aqueous sodium chloride solutions, which is done to a wide extent industrially today. As already stated, the winning of pure sodium from this has been relatively difficult and involved. The invention opens a new path to the direct winning of pure sodium from this sodium amalgam, by using the new electrolyte. From the possibility of performing the electrolysis at considerably lower temperatures than before, but with at least equally favorable conditions with respect to current efficiency, it is possible, with the invention, to obtain pure sodium in a single process, and it need not be subjected to further involved purification.

The purity of the cathodically deposited sodium is also improved due to the possibility of keeping the bath temperature relatively low. In particular, the sodium amalgam used in / 8
this embodiment of the invention is an amalgam such as occurs in the electrolytic preparation of alkyls of the metals of the second and third to fifth major groups of the periodic system through electrolysis of organoaluminum compounds, as is depicted in the Belgian Patent 590,573.

Sodium amalgam is formed cathodically in such an electrolysis, and it is preferable not to exceed a sodium content of about 1.5% by weight in the amalgam, because then the amalgam, which is still liquid, can be removed simply. In order that the mercury can be re-used for production of the metal alkyls, it must be at least partially freed of its sodium content. This can be done by the process of the invention.

It must be considered extremely surprising that performing the process of the invention with formation of ethyl sodium from sodium amalgam is possible at all. As is well known, mercury is one of the metals which, as anode metals in the electrolysis of organoaluminum complex compounds, forms volatile metal alkyls. Now, as the reactivity of the sodium in the amalgam is considerably reduced in comparison to that of the pure sodium, it could not be predicted that the sodium from the amalgam would be converted into ethyl sodium without simultaneous formation of mercury alkyls. It is also known that one can produce lithium amalgam and mercury alkyls by shaking lithium alkyls with mercury:

$$2\ LiR + Hg \rightleftarrows HgR_2 + Li$$

This is an equilibrium reaction, so that if such a conversion were also to occur with sodium, the smooth dissolution of the sodium out of the amalgam would be impossible.

The attack of the ethyl radical occurs at the surface of the amalgam layer. Thus, the sodium is consumed here, so that the surface is more and more enriched in mercury.

Now if one works with electrolytes $MeAlR_3R'$, in which R' indicates alkyl, alkoxy or aryloxy, and at such high current densities that the formation of sodium alkyl proceeds faster than the diffusion of the sodium from the interior to the surface of the amalgam, undesired formation of mercury alkyls can occur. Thus, it is preferred to use current densities which have upper limits, and in particular, the region of up to about 80 A/dm^2 is preferred. The range of about 10 to about 50 A/dm^2 is especially suitable. One can also prevent the undesired formation of mercury alkyls by stirring the sodium amalgam.

Also, if the amalgam is more and more depleted in sodium during the electrolysis, the danger of undesired mercury alkyl formation becomes greater. This will certainly occur if the last remainder of sodium is removed from the mercury.

In the invention, then, it is preferred not to perform the electrolysis until the sodium is completely removed, but always to leave a sufficient residue of sodium in the amalgam. / 9
But this can be less than 1%, and, for instance, can be 0.2 to 0.5% sodium. This does not limit the applicability of the invention, because the mercury is serving in a cyclic process as a medium to take up the primarily deposited sodium, and any possible residual sodium content is obviously indifferent for such a cyclic process.

In the electrolysis with sodium-containing anodes, the electrolysis can be carried out particularly advantageously with electrolytes of the general formula $MeAlR_3R'$, in which R has the given meaning and R' is hydrogen. In the electrolysis

of these compounds it is not the ethyl residue but the hydrogen residue which is anodically bound to the sodium going into solution. But as long as this reaction of the hydrogen is preferred to the corresponding reaction of the ethyl residue, danger of undesired formation of mercury compounds is excluded. Sodium hydride can be formed, and from it, the corresponding complex electrolyte compound (through reaction with the aluminum-containing compound simultaneously liberated anodically from the decomposition of the electrolyte). But mercury hydride cannot be formed. The hydride-containing electrolyte can also be electrolyzed advantageously at indifferent anodes. As long as these do not exhibit such an over-voltage for hydrogen that the discharge of the ethyl residue proceeds more easily, then hydrogen is formed anodically instead of the gaseous decomposition products of the ethyl residue. This can be re-used simply in the regeneration of the electrolyte. In the case of use of anode metals from the second to the fifth groups of the periodic system, which are converted into the corresponding alkyls during the electrolysis, the use of the hydride-containing complex is less suitable, because here other undesired side reactions can occur in the electrolyte.

In one particularly simple and preferred embodiment of this modification of the process, the electrolysis is carried out as a "three-layer process". In this case, the dense sodium amalgam is the lower layer; the fused electrolyte is the middle layer, and any indifferent metal cathode, perhaps in the form of a network, is applied to the surface of the electrolyte. The sodium deposits around this. Now it has been found, to be sure, that the sodium has a higher specific gravity than the fused electrolyte, so that, if the electrolysis is carried out at temperatures at which the sodium is present as the molten metal, this molten metal

would drop down through the electrolyte onto the amalgam anode. This would make the process difficult. This problem is countered in another preferred embodiment of the invention in the following manner:

The density differences between the fused electrolytes and the sodium are not very great. They are approximately 0.05 to 0.1. That is, in the electrolytes the sodium has only one twentieth to one tenth of its actual density. Also, the surface tension of the molten sodium in the fused electrolytes is very great. Therefore, very strong surface or capillary forces occur at the boundaries between the sodium / 10
and the electrolyte. The result of this is that a quite coarse network of a suitable insulating material placed horizontally in the electrolyte a few millimeters above the mercury surface is entirely sufficient to keep a sodium layer as much as several centimeters thick completely suspended, and to keep it from sinking down. The surface tension prevents the sodium from passing through the net. The net itself can consist of cellulose fibers, or, better, of a glass fiber cloth. It is possible to operate at voltages of about 1 volt or even lower.

Corresponding systems can also be used in the process of the invention.

It is basically preferred, in carrying out the process of the invention, to work at temperatures at which the sodium is separated as a liquid at the cathode. As the melting point of sodium is 97°C, temperatures of at least 100°C are preferred, and in particular the temperature range from about 100° to 150°C. The lower temperatures are used for production of especially pure sodium, so that even working above 100°C with single electrolysis, it is possible to

obtain sodium containing only 0.03 to 0.05% mercury. But the use of temperatures below 100°C is also within the range of the invention. At these temperatures, the mercury content of the separated sodium can be reduced even further. But, as temperatures above 100°C simplify the processing and favor the current yield, it is particularly advantageous to use the given temperature range.

If particularly high purity in the cathodically deposited sodium is desired, it can also be attained by repeating the electrolysis described. In this case, the sodium deposited in the first electrolysis is connected as an anode and subjected to further refinement. Such double electrolysis can be done simply in only one cell in which one more net is placed between the cathode and anode of the previously described three-layer electrolysis. The space above and below this central sodium layer is filled with electrolyte, so that when the current flows, the underside of this intermediate sodium layer acts as the cathode and the upper side acts as the anode. In this way, the raw sodium from the sodium amalgam is first separated in the intermediate layer. Finally, at the upper cathode, pure sodium precipitates with some 1 γ of foreign metal per gram of sodium, due to the repeated electrical refining of the central crude sodium layer. As the distance between the cathode and anode need always be no more than a few millimeters, the power requirement for such a double cell is hardly increased above a single cell. Relatively low voltages, such as 0.5 to 5 volts, can be used in the process.

If indifferent electrodes are used in the process of the invention, i. e., if no sodium ethyl or any other metal alkyl / 11
forms, the process can be carried out in any arbitrary

electrolysis cell as long is care is taken that no electrically conducting connection forms between the cathode and the anode, as from the sodium metal being separated. The drawing shows a system in which the process of the invention can be carried out using anodes of metal-alkyl-forming metals of the second to the fifth groups of the periodic system. The electrolysis cell shown here contains an opening, 1, through which the electrolyte, preferably in the melted state, can be introduced. The metal, for which the metal alkyl is simultaneously formed, is introduced through opening 2, in the form of small spheres, for instance, or as a granulate. During the electrolysis the sodium deposits in a thin layer on the cylindrical cathode, 8, of copper, for example, in the center of the electrolysis vessel. The sodium runs down and can be removed from the electrolysis cell through opening 3. The cathode space is separated from the anode space by a perforated cylinder, 7, of insulating material and a diaphragm laid on it. This can, for instance, consist of hardened filter paper or of a fine fabric or glass filter cloth. Outside of it is the anode space, which is filled with metal spherules, 11, which become covered continuously with fresh metal corresponding to the amount of metal dissolved in the electrolysis. This anode space has two removal openings, 4 and 6, through which the metal alkyl formed can be removed, depending on whether it sinks or rises in the electrolyte. The cathode liquid is in the interior of the perforated cylinder, 7. It can be removed from the apparatus through the overflow, 5. The cathode cylinder, 8, can be filled internally with a heating or cooling fluid, the temperature of which is regulated by the heating element, 9. Thus it is possible to regulate the temperature of the cathode liquid in the desired manner, while the temperature of the anode liquid can be adjusted by the heating element 10, shown here as a circulating liquid heater.

Example 1

In an electrolysis cell of enameled steel plate, with the shape of a closed boiler, there is a cathode of copper plate in the center, extending to the bottom of the vessel. At both sides, at a distance of 1 to 2 cm, are anodes, also of copper plate, at least 10 to 20 cm shorter than the cathode. The vessel is filled, under nitrogen, with a molten mixture of 80% potassium aluminum tetraethyl and 20% sodium aluminum tetraethyl. Also, a large amount of sodium butoxy aluminum triethyl is prepared, according to the French Patent 1,223,643.

The electrolysis is done at 140°C and at a current density of 30 A/dm^2. Before one turns on the current, one allows a small amount of the molten butoxy complex to flow into the electrolyte until its content in the mixture is about 5%. Now one turns the current on, and lets 7.85 g sodium butoxy aluminum triethyl to flow continuously into the electrolyte per ampere-hour. The fused sodium separates at the cathode in / 12
the proper amount, i. e., 0.86 g/Ah. It flows down the cathode and collects as a confluent layer at the bottom of the vessel, where it can be drawn off. A 1:1 mixture of ethylene and ethane forms at the anode. Above the electrolyte, a layer consisting of pure butoxyaluminum diethyl collects. This can easily be separated and converted back to sodium butoxy aluminum triethyl as described in French Patent 1,223,643, using sodium hydride and ethylene. It can be added back to the electrolyte. In the electrolysis, care should be taken that there is always a certain amount of the complex sodium butoxy triethyl aluminum in the electrolyte. A very small steady content is sufficient in itself. But, as the addition is not always exactly equivalent to the current flow because of occasional current vatiations, it is practical

to work with a content of a few percent of the alkoxy compound in the electrolyte.

Example 2

3,320 g (= 20 moles) of sodium aluminum tetraethyl are stirred for 5 hours at 150°C with 740 g (10 moles) of potassium chloride. After the sodium chloride formed has settled, the equimolar mixture of sodium aluminum tetraethyl and potassium aluminum tetraethyl formed is electrolyzed in the apparatus in the figure with a lead anode. The cathode is a copper cylinder. At a distance of/1 cm is a perforated cylinder made of a material resistant to the electrolyte and electrically nonconducting, such as porcelain, or cloth-reinforced Bakelite. A diaphram of hardened filter paper or of a fine fabric or glass filter cloth is stretched around this cylinder. Behind the diaphragm is the anode space, which is filled with lead spherules, and which can be loaded continuously with lead spheres, corresponding to the lead dissolved in the electrolysis. Heating of the electrolyte, or removal of the current heat generated during the electrolysis is provided by circulating a liquid at 100°C in the interior of the closed cathode cylinder. The input or removal of heat at the outer jacket of the cylinder is controlled so that the temperature in the anode space does not exceed 70°C. During electrolysis, it is convenient to have the temperature in the cathode space about 100°C and that in the anode space 70°C. The conductivity of the mixture used is $4.5 \cdot 10^{-2}$ $(\Omega \cdot cm)^{-1}$ at 100 °C. The current is adjusted to 20 A, corresponding to a cell voltage of 2 volts.

The sodium formed at the cathode flows down the surface of the cathode in a thin film to the lower cathode space, where it can be drawn off molten from time to time. The

flow out of the anode space is adjusted so that a reaction mixture with 10% tetraethyl lead runs out. This is the case if some 500 cm^3 of liquid is removed from the anode space per hour. The input of sodium aluminum tetraethyl into the cathode space should be regulated so that the liquid level in the cathode space is 4 to 5 cm higher than in the anode space.

The yield of sodium is 23 g sodium per 26.8 ampere hours /13
(= 100% of theory).

Example 3

Fused sodium aluminum tetrabutyl is electrolyzed at 120°C in the apparatus described in example 2, using aluminum granules as the anode material. The cathodically formed sodium collects at the bottom of the cathode space, and can be removed there from time to time. Otherwise, one operates similarly to the manner described in example 2, with the difference that one removes a mixture with 10% aluminum tributyl from the anode space. This is freed of aluminum tributyl in a vacuum at 100°C and 0.1 Torr.

The yield of sodium is 23 g sodium per 26.8 ampere hours (= 100% of theory).

Example 4

The electrolysis is done in the apparatus shown in the figure and described in example 2, but the anode space is not filled with metal granules. Instead, a cylinder of metal wire, such as copper, is fastened in the anode space. The electrolysis temperature is 100°C. As the electrolyte, one uses a melt of the complex compound, sodium aluminum triethyl hydride. A current of 15 A is adjusted with a terminal

voltage of 6 volts. Then 12.8 g sodium deposit cathodically per hour (= 100% of theory), and 6.3 liters of hydrogen gas form anodically. The inflow of sodium aluminum triethyl hydride into the cathode space is adjusted with the outflow from the anode space so that a level difference of 4 to 5 cm is maintained between the liquid levels in the cathode space and the anode space.

The outflow from the anode space is collected and freed of triethyl aluminum in a vacuum of 1 mm Hg at 100°C. The distillation residue can be returned to the electrolysis cell. The hydrogen formed anodically can be used in the regeneration of the aluminum triethyl to the complex $NaAl(C_2H_5)_3H$. The triethyl aluminum is converted into sodium aluminum triethyl hydride with NaH at 100°C, and this can be reused in the electrolysis.

Example 5

A cylindrical steel vessel, enameled on the inside, is used as the electrolysis cell. The raw sodium to be refined is present on the bottom in the molten state. A cylinder of somewhat smaller diameter, of enameled steel plate, with an opening at each end, is hung in the vessel. A coarse mesh of glass fiber cloth, with a distance of 1 to 3 mm between meshes, is stretched tightly horizontally across the lower opening. The mesh is 3 to 5 mm above the surface of the liquid sodium. Just above the mesh is a mesh of copper or iron wire as the cathode. Electrolysis temperature is 150°C. Sodium aluminum tetraethyl is used as the electrolyte. The electrolyte melt must stand above the upper edge of the hanging cylinder, so that the cathodically separated sodium is surrounded above and below by electrolyte. An electrode

current density of 20 A/dm^2 is maintained with a terminal voltage of 2.0 volts. The cathodically formed sodium collects above the glass fiber mesh and can be removed from this space from time to time. By adding crude sodium during the electrolysis, one ensures that the separation of the anode and cathode is maintained.

The yield of sodium is 23 grams per 26.8 ampere hours. The same amount of current would dissolve 23 grams of sodium anodically. The yield is 100%.

Example 6

One proceeds as described in Example 5, but uses as the electrolyte a mixture of 20% sodium aluminum tetraethyl and 80% potassium aluminum tetraethyl, replacing the liquid crude sodium by the same volume of 1% sodium amalgam. Electrolysis is done at 150°C with a current density of 30 A/dm^2 and a terminal voltage of 1.5 volts. The cathodically separated sodium collects as a confluent liquid layer above the glass fiber mesh. In order to remove the heat from the current and to mix the electrolyte, one allows the electrolyte to circulate through the electrolysis cell from a larger electrolyte supply, holding the height of the liquid in the cell constant. This is easily accomplished if one allows the same volume of electrolyte to flow into the space between anode and cathode from the supply vessel, per unit time, which one pumps back into the supply vessel at the point opposite the input opening. After 185 ampere hours, 160 g sodium separates cathodically. It can be allowed to flow out of the upper part of the electrolysis cell.

The sodium thus obtained still contains some 0.03% Hg. The mercury content goes even lower if a temperature of 120°C

is maintained during the electrolysis. Then one can easily attain 0.01% mercury or less. This is the same mercury content which can only be attained after additional treatment with metallic calcium when the sodium is obtained from sodium amalgam with an electrolyte of fused sodium bromide, iodide or hydroxide. The primary sodium content in this well-known process is of the order of 1%. Even the last traces of mercury can be eliminated if one repeats the electrolysis as in Example 5.

The original 1% sodium amalgam is depleted to about 0.2% Na in the mercury. It is conveniently provided to the cell and, after it is reconcentrated to 1% Na, it can be used for a new electrolysis.

The yield of sodium is 23 g Na per 26.8 ampere hours (= 100% of theory).

Patent Claims

1. Process for cathodic deposition of sodium through electrolysis of sodium-containing organic aluminum compounds in an inert atmosphere, characterized by the fact that a melt of complex compounds having the general formula $MeAlR_3R'$, in which Me is sodium or a mixture of sodium and potassium, R is alkyl residue, and R' is hydrogen, an alkyl, an alkoxy and/or a perhaps substituted aryloxy residue, is electrolyzed, and a reaction of the anodically formed, not complexly bound metal alkyls with the cathodically deposited sodium is prevented, for instance, by using a diaphragm, by electrolysis in vacuum, or by addition of compounds of the general formula $MeAlR_3OR''$, where the Me and R have the stated meaning and R" indicates an alkyl, a cycloalkyl, a phenyl, or an alkyl-substituted phenyl residue. / 15

2. Process according to Claim 1, characterized by the fact that the electrolysis is done with complex compounds of the general formula $MeAlR_3R'$, in which R is a straight-chain alkyl residue with 2 to 6, and especially 2 carbon atoms and R' is hydrogen, a straight-chain alkyl residue with 2 to 6, especially 2 carbon atoms, or the organic residue OR".

3. Process according to claims 1 and 2, characterized by the fact that with use of an electrolyte of mixtures of sodium and potassium complex compounds of the general formula $MeAlR_3R'$ the sodium complex compound is continuously or intermittently added to the electrolyte which is becoming depleted of sodium in such amounts that the proportion of potassium in the electrolyte does not exceed 80%.

4. Process according to Claims 1 to 3, characterized by the fact that electrodes of copper, brass, iron, nickel or other indifferent metals or alloys are used.

5. Process according to claims 1 to 4, characterized by the fact that the electrolysis is done using non-indifferent electrodes under vacuum, so that any free metal alkyl compounds formed anodically are immediately distilled off.

6. Process according to claims 1 to 5, characterized by the fact that the work in vacuum is preferably done at pressures below 1 mm Hg.

7. Process according to claims 1 to 4, characterized by the fact that anodically formed free trialkyl aluminum is converted to alkoxy or aryloxy aluminum dialkyl compounds and complex compounds having the formula $MeAlR_4$ by preferably continuous addition of complex compounds of the general formula $MeAlR_3OR"$.

8. Process according to Claims 1 to 4, characterized by the fact that the electrolysis is done with a sodium-containing anode — of melted crude sodium, for instance — but especially with a sodium amalgam electrode, using particularly sodium amalgam with an initial content of up to about 1.5% sodium by weight.

9. Process according to Claim 8, characterized by the fact that the electrolysis with sodium amalgam as the anode is interrupted at a time when there is still so much sodium in the anode material that formation of mercury alkyls, for instance, is prevented. / 16

10. Process according to Claims 1 to 3 and 8 and 9, characterized by the fact that in the case of sodium-containing or indifferent anodes, the work is done with complex compounds of the formula $MeAlR_3R'$ as the electrolyte, in which R' indicates hydrogen.

11. Process according to Claims 9 and 10, characterized by the fact that the electrolysis is performed up to anodic residual sodium content below 1%, e. g., to some 0.2 to 0.5% sodium.

12. Process according to Claims 8 to 11, characterized by the fact that the current densities are limited to about 80 A/dm^2 during the electrolysis, depending on the rate of diffusion of the sodium in the anode material, so that there is always enough sodium available for formation of alkyl sodium at the anode surface.

13. Process according to Claim 12, characterized by the fact that the electrolysis is done at current densities in the range of 10 to 50 A/dm^2.

14. Process according to Claims 8 to 13, characterized by the fact that the electrolysis is done with the sodium amalgam as the lower layer, the fused electrolyte as the middle layer and the cathodically deposited sodium as the upper layer, kept in suspension by a coarse-mesh net of insulating material such as glass fiber cloth or cellulose fiber cloth.

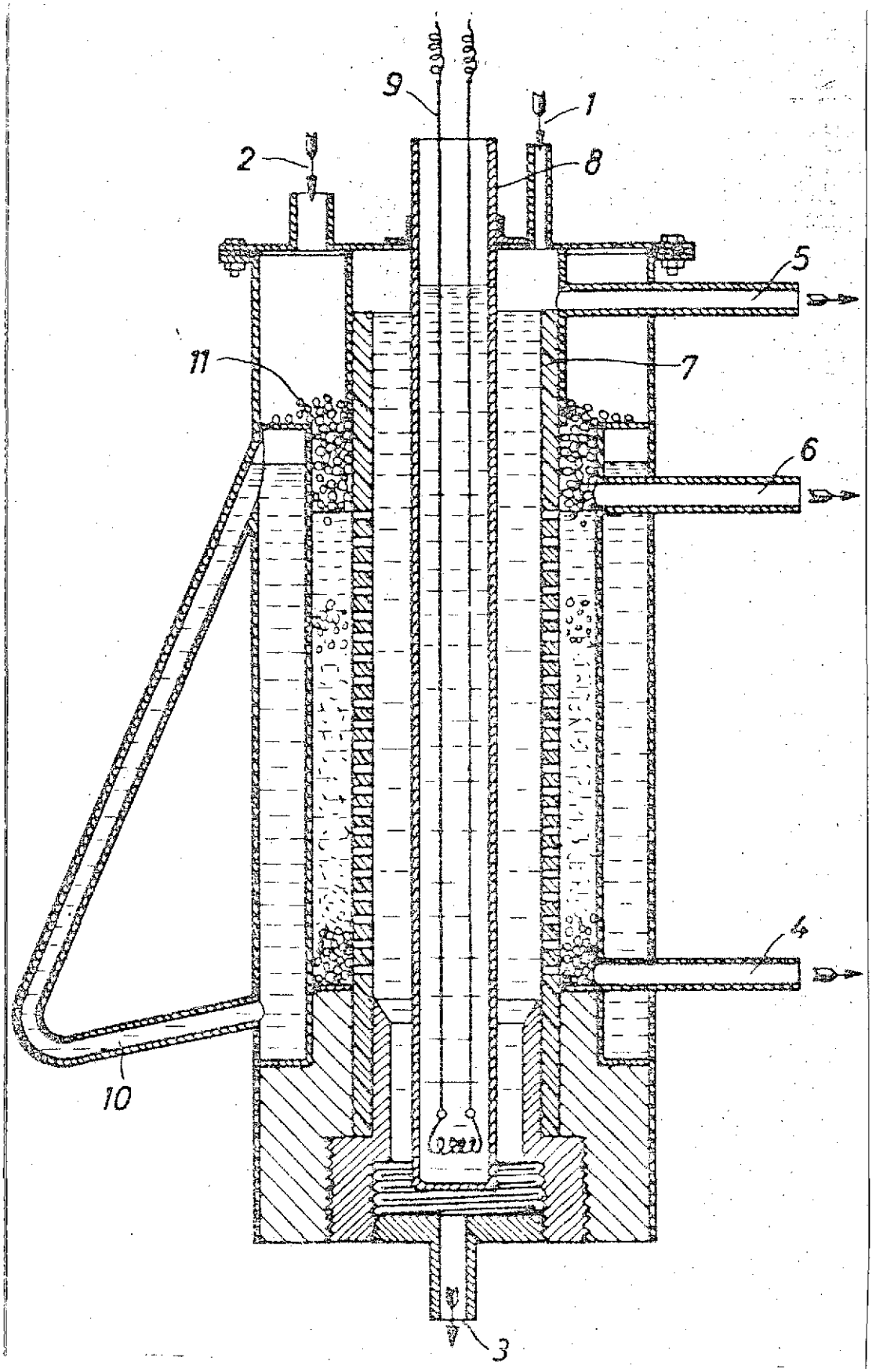
15. Process according to Claim 14, characterized by the fact that the work is done with a coarsely meshed net only a few millimeters above the mercury surface to prevent the sodium layer from sinking down in the electrolysis system.

16. Process according to Claims 1 to 15, characterized by the fact that electrolysis is carried out at temperatures above the melting temperature of sodium, and up to about 150 to 160°C.

17. Process according to Claims 1 to 16, characterized by the fact that in order to obtain very pure sodium, the work is done at lower temperatures, particularly in the range of 100 to 120°C, and particularly with an indifferent metal anode, while the electrolyte being depleted of sodium is held at the desired composition by continuous or intermittent addition of fresh sodium complex compound.

18. Process according to Claims 1 to 17, characterized by the fact that electrolysis is done with voltages in the range of 0.5 to 5 volts.

One page of drawings in addition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